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The electro-chemistry of soil formation: V. A lysimeter study of podzolic solvation and precipitation.[1]

By SANTE MATTSON and ELISAVETA KOUTLER-ANDERSSON.

From the Institute of Pedology.

Introduction.

On the basis of previous investigations (MATTSON & GUSTAFSSON 1935 & 1937; BORATYŃSKI & MATTSON 1939, and MATTSON 1941) the following dominant forms of solvation and precipitation may be assumed to occur in a leached soil.

Solvation:

1. Anionic solvation of soil acidoids (primarily silica and humus) at a pH above the isoelectric point (I. E. P.) of the amphoteric gel complex.
2. Anionic solvation of soil basoids (primarily sesquioxides) in combination with the ionized acidoids at a pH above the I. E. P. of gel complex.
3. Cationic solvation of the soil basoids at a pH below the I. E. P. of the gel complex.
4. Cationic solvation of the acidoids in combination with the ionized basoids at a pH below the I. E. P. of the gel complex.

In addition to these forms of solvation we have to consider the ordinary solubility which in the case of silica is appreciable.

In highly acidoid soils, which have no I. E. P., the sesquioxides are cationically solvated (probably mostly as single Al and Fe ions) at very low pH although the gel complex remains electronegative. The dissociation of the acidoids must be greatly suppressed and the acid hydrolysis of the gel complex must be complete at a very low pH. The charge remains however negative for the same reason that all chemically indifferent materials charge themselves negative in water.

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Precipitation:

1. Isoelectric precipitation of an anionic or a cationic sol complex at a pH corresponding to the I. E. P. (Only the cationic complex is normally thus precipitated in the soil profile in which the pH normally increases downwards.)

2. Isoelectric precipitation of a cationic sol complex by an anionic gel complex. (Precipitation 1 and 2 must be assumed to occur jointly in all podzols.)

3. Isoelectric precipitation of an anionic sol complex by a cationic gel complex. (This form of precipitation is probably quite common in many soils in which an anionic solvate passes through a layer rich in sesquioxide and having a pH low enough to ionize many of the basoid groups on the gel complex. Under conditions of a high pH in the B horizon the anionic sol complex cannot be expected to be precipitated.)

In order to find out how the solvation and precipitation in podzolic materials actually takes place and in order to determine some of the factors which influence the process we have carried out a series of experiments with laboratory lysimeters in which materials from the different horizons of a podzol profile were placed in separate layers and leached with water as well as with dilute salt solutions. The following is a report of the results thus far obtained.

Experimental part.

The lysimeters consisted of sintered glass filter tubes. N:o G 2 (Schott u. Gen. Jena) 25 cm. high and 7 cm. in diameter (cf. fig. 48). The soil material was from the Häggbygget podzol profile (MATTSON & HOU 1937).

Samples of 150 grams of mineral soil from horizons A_2, B_1, B_2 and B_3 were slightly moistened (to insure a uniform distribution of the particles) and placed in layers each containing 150 grams. A layer of coarsely ground organic matter (V = vegetation; F = litter; H = humus) was then placed on top of the mineral soil. In one series the samples were mixed and placed together in a single layer as when a soil is cultivated, and in another series the mineral layers were placed »upside down» as compared to their natural order of sequence.

Each series consisted of as many lysimeters as the number of layers included in the study. Thus the first tube contained the humus alone; the second the humus + A_2; the third humus + A_2, + B, and so forth. It was later found desirable to continue some of the series with several layers of B_3 (cf. tables). By this arrangement it was possible to determine the solvation and precipitation

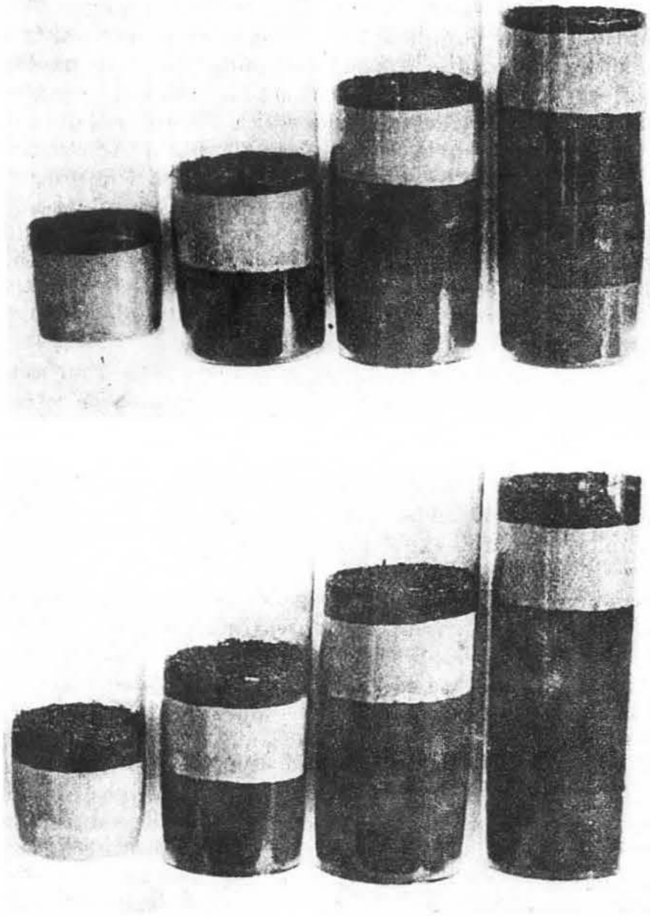

Fig. 48. Lysimeter series with 5 grams humus (above) and 12.5 grams humus (below). Mineral layers A_2, B_1, B_2, and B_3 each 150 grams soil.

in each layer on the assumption that the solvates from the same layers had the same composition in all of the lysimeters.

The combination of the different series studied is shown in table 24 column 2. In the complete series the humus consists of one fifth F-sample placed on top of four fifths H-sample. Double series with 50, 12.5 and 5 grams humus were made up, one of which was leached with distilled water (series A, B and C) and the others with N. 0.01 (D) or N. 0.001 (E and F) $CaCl_2$ solution. In series

G the mineral layers are placed »upside-down» and in series H the samples were all mixed and placed in single layers.

In addition to the complete series containing material from every horizon in the soil profile, special combinations were made in some of the series. Thus systems 10 and 11 in series A contain only H and V samples, respectively, in place of F:H and should be compared to system 8. System A 9 contains only B_3 in the mineral layers. In series E_{II} we have an extra series in which the mineral layers are built up of B_3 samples alone. In series H, samples A_2 and B_1 have been replaced by the more basic B_2 and B_3 (system 5), F+H has been replaced by V (6) and by H (7) and in system 8 the humus layer has been omitted.

Of the mineral samples the B_3 is the most basic (strongest basoid) ($pH_u = 4.78$) and A_2 the least basic ($pH_u = 3.86$). B_1 ($pH_u = 3.92$) and B_2 ($pH_u = 4.51$) occupy, with respect to their amphoteric properties, intermediate positions. The B_1 sample is coffee brown (when wet) and contains 9.58 percent organic matter (loss on ignition), B_2 is rusty brown and has 7.48 percent, B_3 is brownish yellow with 3.61 percent and A_2 is very light gray and has 1.52 percent organic matter. The acid-oxalate soluble sesquioxides in other samples from the same profile are reported by MATTSON and HOU.[1]

The leaching was carried out at the rate of 10 cc water or solution four times weekly and the solvates were collected in 200 cc volumetric flasks to which a few drops of toluol was added. When 200 cc had been collected the solution was divided into two equal parts. One part was used for the determination of the pH, the acidity, the loss on ignition of the solid matter, and the »excess base» in the ignited residue. The other part was reserved for a final determination of silica, sesquioxides, manganese and calcium. After five to six months 600 cc had been collected and analysed. Table 24 gives the sum of the various substances present in 600 cc.

We had planned to continue the leaching until a second 600 cc volume had been obtained and we did continue several of the series for a considerable time after the first 600 cc had been collected but we finally decided to stop the experiment and for the following reasons.

1. The pH increased in most cases considerably above the pH of the first solvate. This was probably due to a decomposition of the organic acids (cf. MATTSON and ANDERSSON 1941).

2. The basoids in the lower layers (B_2 and B_3) did not adsorb the dark colored humus acidoids as efficiently as during the first part of the experiment as evidenced by the color of the solvates.

[1] Al_2O_3: $A_2 = 0.65$, $B_1 = 1.89$, $B_2 = 2.13$, $B_3 = 1.93$.
Fe_2O_3: $A_2 = 0.26$, $B_1 = 3.44$, $B_2 = 3.76$, $B_3 = 1.64$.

This was probably partly due to the higher pH and partly to a progressive saturation of the basoids with acidoids.

3. A number of small flies developed in some of lysimeters and these produced an evident effect on the solvates which turned darker.

4. Some of the systems became clogged.

The reason why these changes were so rapidly brought about, must depend on the great chemical and biological activity of our systems as compared to the conditions in the natural soil profile. In the latter the chemical potential or affinity, as for examples that of the acidoid/basoid relationship, has a smooth gradient; the system has had time to level out the potential differences to a minimum and to *approach* (never attaining) an equilibrium between the colloid complex and soil solution. The chemical action taking place as a result of the movement and change in composition of the soil solution will therefore be infinitesimal at any one point, spread out it is with respect to both time and space.

In our systems there is no such smooth gradient for even within a single layer the colloids from the lower part of a soil horizon are brought in contact, by the mixing, with the colloids of the upper part whose acid-base affinities may differ considerably. This mixed material, which is rich in polar groups, is heterogenic both with respect to the acid-base and to the oxidation-reduction relationship.

Because of this great activity of the disturbed soil materials we have now come to the conclusion that a study of the chemical reactions of such materials by the method here employed ought to be carried out after the complete exclusion of all biological factors by working under sterile conditions. We shall therefore continue the work along these lines and include a variety of combinations of soil materials.

Despite evident complications due to biological influences the results of the experiments bring out some very definite information. We shall now turn to a discussion of the results which are shown in table 24 and in fig. 49 to 52.

The color. It will be noted that the color, which is chiefly due to the presence of humus acidoids, is most intense in the solvates from the A_2 and B_1 layers whereas the more basoidal B_2 and B_3 layers remove the color, i.e., bind the humus acidoids. In series D the high Ca ion concentration did not permit any appreciable solvation of humus.

The pH. The pH values given in the table are those of the first 200 cc solvate which contained the largest quantities of materials. In the water systems the pH fluctuated considerably but in the $CaCl_2$ systems it was more constant. We note that the pH increases as the solvate passes the basic B_2 and B_3 layers. The in-

Table 24 a. *The composition of the solvates (600 cc) from the lysimeters funnels, obtained by leaching with water.*

A_2, B_1, B_2 and B_3 each = 150 g. in every system.

No.	Layers	SiO_2 mg.	Al_2O_3 mg.	Fe_2O_3 mg.	MnO mg.	CaO mg.	Loss on ignition mg.	Excess base m. e.	Acidity m. e.	pH	Color[1]
	Series A:— Humus layer = 50 grams FH (= 10 g. F on 40 g. H).										
1	V (10 g.)	8.8	2.7	2.3	2.2	12.5	542	.96	.38	5.49	d. br.
2	V : H (10 : 40 g.)	14.2	3.3	2.7	trace	7.0	857	.33	1.15	3.87	br.
3	F (10 g.)	4.2	1.3	1.7	»	7.4	231	.24	.17	5.55	y. br.
4	F : H	8.6	.9	1.9	»	3.5	533	.00	.82	4.04	y. br.
5	F : H : A_2	(27.2)	22.9	15.6	»	5.6	637	.04	.81	4.13	d. br.
6	F : H : A_2 : B_1	12.6	14.3	48.5	»	4.2	589	.07	1.01	4.09	br.
7	F : H : A_2 : B_1 : B_2	17.1	23.5	33.2	»	3.7	372	.04	.73	4.19	l. br.
8	F : H : A_2 : B_1 : B_2 : B_3	7.7	.9	3.4	1.3	3.8	186	.12	.37	4.69	0
9	F : H 4 B_3	7.4	.2	.0	1.3	2.8	100	.06	.10	4.86	0
10	H[2] : A_2 : B_1 : B_2 : B_3	6.5	.2	2.7	trace	3.4	149	.16	.14	4.61	0
11	V[2] : A_2 : B_1 : B_2 : B_3	8.2	10.2	60.4	2.0	6.4	460	.24	1.51	4.34	trace
	Series B:— Humus layer = 12.5 g. FH (= 2.5 g F on 10 g. H).										
1	F : H	2.8	.7	1.5	trace	2.5	246	.00	.43	4.47	y. br.
2	F : H : A_2	(51.0)	21.2	18.8	»	3.3	309	.00	.32	4.42	d. br.
3	F : H : A_2 : B_1	17.2	5.1	13.7	»	3.5	251	.00	.42	4.40	l. br.
4	F : H : A_2 : B_1 : B_2	8.9	2.1	5.3	»	3.2	190	.00	.27	4.46	l. y.
5	F : H : A_2 : B_1 : B_2 : B_3	5.8	.6	2.3	.3	3.8	120	.06	.13	4.75	0
	Series C:— Humus layer = 5 g. FH (= 1 g. F on 4 g. H).										
1	F : H	6.8	.8	1.6	trace	2.5	241	.00	.26	4.43	y. br.
2	F : H : A_2	(63.2)	21.5	16.1	»	2.4	492	.02	.43	4.51	d. br.
3	F : H : A_2 : B_1	9.8	9.6	19.4	»	2.5	372	.00	.55	4.35	l. br.
4	F : H : A_2 : B_1 : B_2	8.8	1.9	5.5	»	2.4	215	.00	.29	4.53	l. y.
5	F : H : A_1 : B_1 : B_2 : B_3	7.8	1.4	4.8	.2	2.8	144	.00	.21	4.61	0
6	F : H : A_1 : B_1 : B_2 : 2 B_3	7.0	.6	1.3	1.8	3.9	164	.00	.14	4.84	0

dividual pH values are not reliable. Thus the pH in system A 1 (V sample rich in organic acids) mounted as high as 7.13 in one of the solvates. We have reasons to believe that some of the organic acids suffered decomposition when the solvate was exposed to the air on the bottom side of the glass filter.

The loss on ignition. This represents four major components: 1. Water. This component is highest where sesquioxides and si-

[1] d. br. = dark brown; y. br. = yellowish brown; l. br. = light brown; l. y. = light yellow; 0 = colorless.

[2] 50 grams.

Table 24 b. *The composition of the solvates (600 cc) from the lysimeter funnels, obtained by leaching with $CaCl_2$ solution.*

No.	Layers	SiO_2 mg.	Al_2O_3 mg.	Fe_2O_3 mg.	MnO mg.	CaO mg.	Loss on ignition mg.	Excess base m. e.	Acidity m. e.	pH	Color
	Series D:— Humus layer = 50 grams FH (= 10 g. F on 40 g. H). $CaCl_2$ = n. 0.01.										
1	F : H	11.0	8.5	6.3	8.2	74.2	554	1.66	1.00	3.53	y.
2	F : H : A_2	(17.1)	13.0	43.7	2.6	61.0	559	1.50	1.48	3.65	y.
3	F : H : A_2 : B_1	13.5	8.3	172.9	.7	11.0	572	.30	4.48	3.82	trace
4	F : H : A_2 : B_1 : B_2	9.4	12.8	173.2	1.0	10.2	510	.26	4.61	3.87	»
5	F : H : A_2 : B_1 : B_2 : B_3	9.1	23.5	153.9	2.3	11.1	482	.42	4.64	4.11	»
6	F : H : A_2 : B_1 : B_2 : 2 B_3	9.6	23.6	145.5	4.6	13.9	490	.28	4.32	4.20	0
7	F : H : A_2 : B_1 : B_2 : 4 B_3	8.6	13.9	21.3	4.6	15.7	391	.98	1.09	4.31	0
I	Series E (I & II): Humus layer = 12.5 g. $CaCl_2$ = n. 0.001.										
1	F : H	4.0	1.3		.7	9.9	288	.08	.40	4.33	y.
2	F : H : A_2	(37.6)	18.8	11.6	.3	2.8	404	.00	.51	4.13	br.
3	F : H : A_2 : B_1	10.8	16.5	45.9	.3	3.4	544	.00	1.38	4.16	br.
4	F : H : A_2 : B_1 : B_2	8.4	9.9	36.0	.5	3.4	342	.00	1.15	4.33	y.
5	F : H : A_2 : B_1 : B_2 : B_3	5.2	4.1	4.2	.9	5.1	168	.08	.37	4.44	0
6	F : H : A_2 : B_1 : B_2 : 2 B_3	8.6	.0	5.8	2.2	5.6	168	.08	.38	4.53	0
II											
1	F : H : B_3	9.0	3.2		1.1	3.3	119	.00	.17	4.55	0
2	F : H : 2 B_3	8.2	1.4	12.2	2.3	3.5	120	.06	.29	4.49	0
3	F : H : 3 B_3	6.8	.4	10.8	n. d.	5.2	175	.10	.14	4.54	0
4	F : H : 4 B_3	7.0	2.4	5.0	1.9	4.2	154	.12	.13	4.74	0
5	F : H : 5 B_3	6.4	1.3		1.8	4.7	118	.06	.16	4.64	0
	Series F:— Humus layer = 5 g. $CaCl_2$ = n. 0.001.										
1	F : H	1.8	0.8		.5	10.9	141	.00	.19	4.62	y.
2	F : H : A_2	(30.6)	4.7	8.3	.3	3.9	156	.00	.24	4.41	l. br.
3	F : H : A_2 : B_1	10.0	21.2	71.4	.5	3.7	530	.00	1.56	4.24	br.
4	F : H : A_2 : B_1 : B_2	11.0	1.2	7.8	.5	4.3	195	.06	.41	4.26	l. br.
5	F : H : A_2 : B_1 : B_2 : B_3	8.6	6.5	11.1	1.4	4.6	212	.04	.71	4.08	y.
6	F : H : A_2 : B_1 : B_2 : 2 B_3	8.2	1.6		.9	5.6	171	.14	.17	4.73	0

lica are high: 2. Nonacidic organic matter. 3. Simple organic acids. 4. Humus acidoids. That the latter comprise only a moderate part of the loss on ignition is evident by the fact that this loss is often very high even in the colorless solvates (cf. especially series D). We note that the loss on ignition in the water systems shows a maximum after the solvates have passed the A_2 layer whereas in the $CaCl_2$ systems it increases until the B_1 layer has been passed. B_1 is rich in Fe-humate and the exchange acidity developed by the salt solution causes an extensive cationic solva-

Table 24 c. *The composition of the solvates (600 cc) from the lysimeter funnels, obtained by leaching with water.*

No.	Layers	SiO_2 mg.	Al_2O_3 mg.	Fe_2O_3 mg.	MnO mg.	CaO mg.	Loss on ignition mg.	Excess base m. e.	Acidity m. e.	pH	Color
	Series G:— Same as series A but the mineral soil layers are inverted.										
1	F : H	8.6	.9	1.9	trace	3.5	533	.00	.82	4.04	y. br.
2	F : H : B_3	11.0	9.3	1.7	»	1.8	221	.00	.19	4.79	0
3	F : H : B_3 : B_2	10.0	6.3	9.5	»	3.5	217	.00	.38	4.20	l. y.
4	F : H : B_3 : B_2 : B_1	9.6	4.2	14.5	»	4.6	269	.10	.57	4.06	l. y.
5	F : H : B_3 : B_2 : B_1 : A_2	8.4	1.1	1.1	»	1.3	282	.06	.35	4.08	y. br.
	Series H:— Same as A but the samples were mixed and placed in a single layer.										
1	F + H + A_2	20.6	7.5	4.7	.7	9.0	701	.07	.99	4.16	d. br.
2	F + H + A_2 + B_1	22.8	27.6	65.5	1.0	16.4	926	.16	1.81	4.08	d. br.
3	F + H + A_2 + B_1 + B_2	33.6	17.3	27.6	1.0	13.7	600	.28	1.03	4.42	y. br.
4	F + H + A_2 + B_1 + B_2 + B_3	56.4	7.4	17.1	.7	11.9	394	.15	.57	4.51	y.
5	F + H + 2 B_2 + 2 B_3	30.7	5.1	34.5	1.0	11.2	386	.28	.55	4.73	l. y.
6	V[1] + A_2 + B_1 + B_2 + B_3	42.9	20.2	22.7	7.9	33.0	749	2.06	.90	4.72	y. br.
7	H[1] + A_2 + B_1 + B_2 + B_3	66.2	7.6	10.6	trace	10.8	402	.30	.64	4.39	y.
8	A_2 + B_1 + B_2 + B_3	18.6	11.2	12.1	»	4.2	174	.04	.29	4.42	l. y.

tion of this complex. In series G the loss on ignition decreases greatly in the uppermost mineral layer which here consists of the strongly basoidal B_3 material. The dark colored humus acidoids are evidently precipitated by combining with the basoids in the gel complex. Note that the loss on ignition and the color again increase in the lower, more acidic layers of the G series.

The »excess base». This is very low in most of the series. It is highest in the organic layers in which it is mobilized by the N. 0.01 $CaCl_2$ solution (D). The mixing of the layers has also caused a considerable increase in the »excess base».

The acidity. This is high in the organic layers but increases in all the series until the solvate has passed the B_1 layer. In series D it is very high and does not decrease until the solvate has passed several B_3 layers. In the water series the acidity reaches the highest value in the mixed series (H 2).

Silica. This constituent shows no particular trend except in the mixed series H (cf. fig. 52 and discussion thereof). It should here only be pointed out that the solvates from the A_2 layer in all the series, except series G, showed a fine crystalline white sediment

[1] 50 grams.

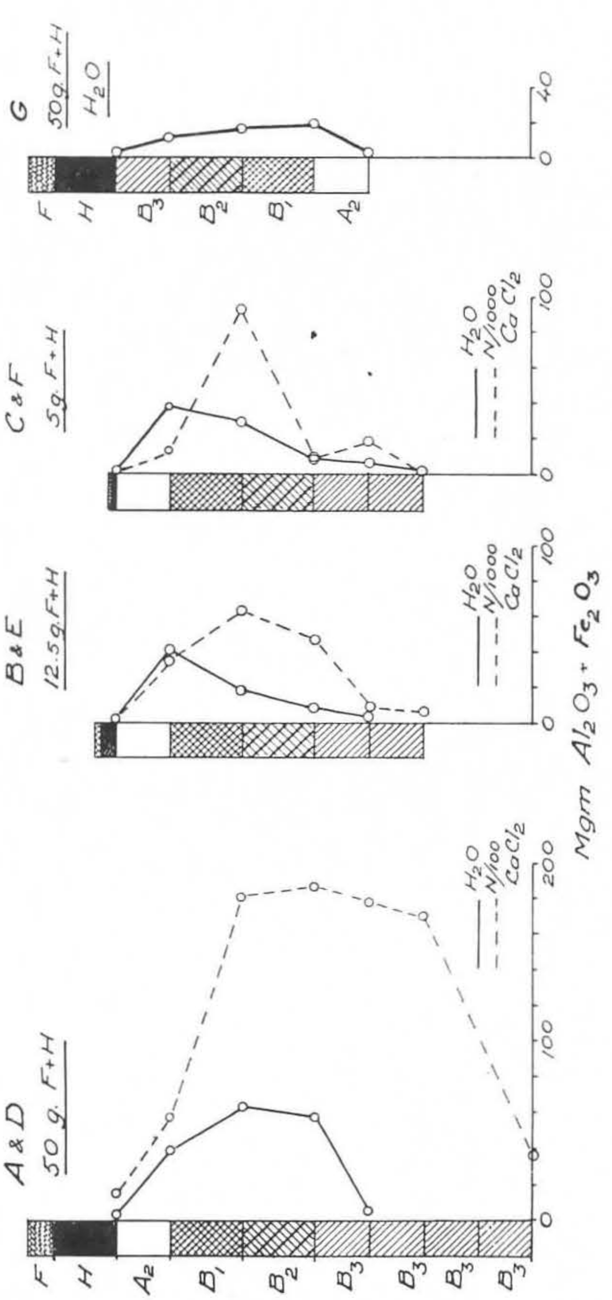

Fig. 49. The amounts of sesquioxides in the solvates from series with different thickness of humus layer when leached with water and with dilute salt solutions (cf. table 24 a & b).

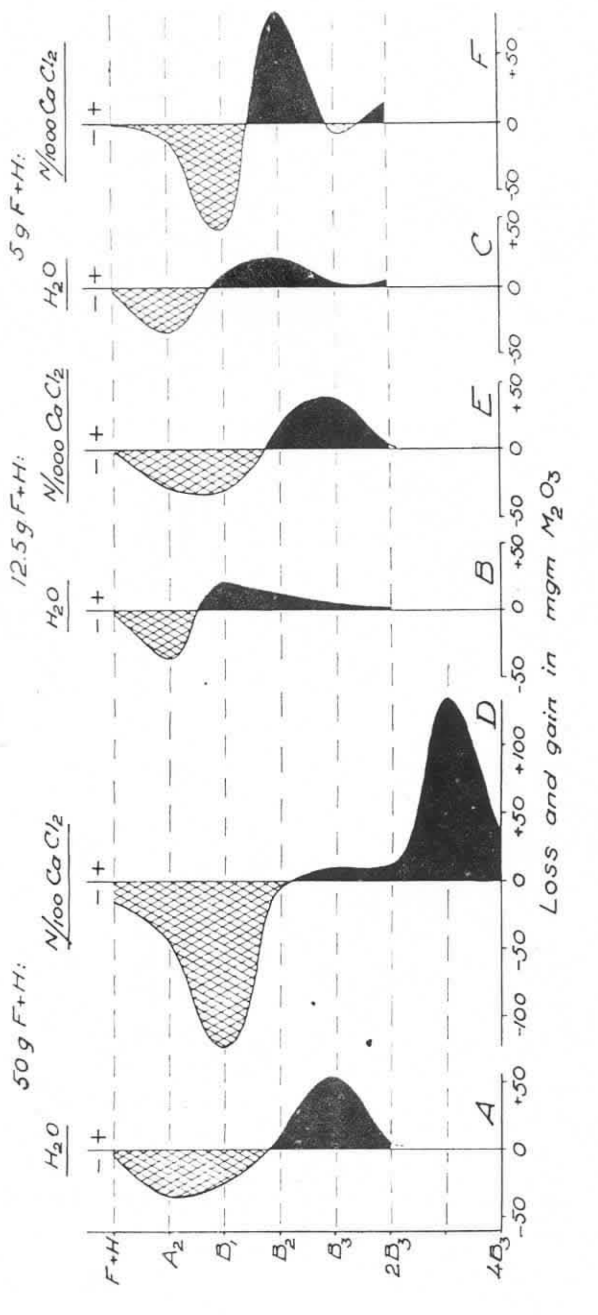

Fig. 50. The same as fig. 50 but showing the eluviation (loss) and illuviation (gain) of sesquioxides in the various layers.

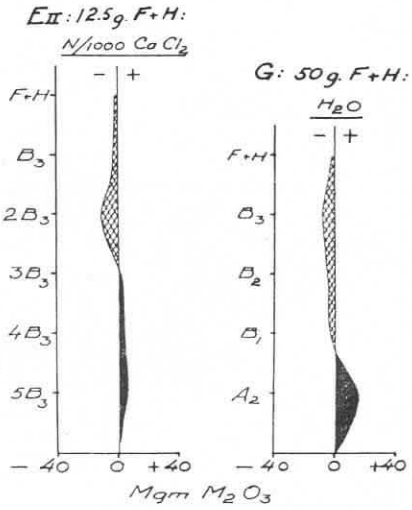

Fig. 51. The same data as in fig. 50 for a series (E II) in which all the mineral layers consist of B_3 (table 24 b), and for a series (G) in which the mineral layers are placed »upside-down» (table 24 c).

which probably was quartz. The unusually high silica values in these cases have been put in parantheses in the table.

Calcium. This element shows no particular trend in the layers of the water series where it is mobilized to a slight extent. In the mixed series it is mobilized to a much greater extent especially in the most acid system H 2 (= 16.4 mgm). The greatest amount of Ca is found in H 6 (= 33.0 mgm) in which the humus was replaced by organic matter from the living vegetation. In the $CaCl_2$ series most of the Ca is adsorbed by exchange in the upper layers.

Manganese. In the water series this element appears only in traces except in the solvates from the B_3 layer in which measurable amounts were found. In the mixed series Mn, like all the other constituents, shows a great increase. The V sample, which is rich in Mn, causes a very great mobilization of this element (7.9 mgm) when mixed with the mineral samples. The relatively large amount of Mn in the $CaCl_2$ series indicates that this element is, at least in part, present in the exchangeable condition, i.e., as divalent Mn cations.

Aluminum and iron. In the »regular» series (A to F) there is a maximum of these elements in the solvates from the A_2 layer in series B and C and in the solvates from the B_1 layer in series A, E_I and F. In series D the maximum, which is here very heavy and extensive, occurs in the still deeper layers. It is thus evident that the solvation of these elements penetrates deeper the thicker the humus layer or the higher the concentration of the salt. This is more clearly brought out in fig. 49.

In the inverted series G there is a maximum of aluminum in the solvate from the uppermost mineral layer (B_3) and a maximum of iron in the solvate from the third mineral layer (B_1). In the mixed series H there is a maximum of both aluminum and iron after the addition of B_1.

We note that considerably more iron than aluminum is solvated and that aluminum is not always the first to attain a maximum as might be expected if the iron were present exclusively in the

ferric condition. We believe, however, the iron to be present chiefly in the ferrous condition. Frequent tests always indicated the presence of much ferrous iron, a fact which we think will account for the observed relationships. Ferrous iron, or ferric iron reduced to the ferrous condition, ought to solvate before aluminum (cf. BORATYŃSKI and MATTSON) and aluminum ought to solvate before ferric iron all according to the electrokinetic behavior of their compounds with soil acidoids. If we add a ferric solution to a soil containing active Al we get chiefly Al in the filtrate, provided that no reduction takes place. In our very active systems strongly reducing conditions must have prevailed. The ionization of mere traces of ferric iron would be sufficient to account for the solvation of this element if we assume an immediate reduction to the much more basic ferrous condition.

The precipitation of aluminum and iron is, in a general way, accompanied by a decrease in the loss on ignition, in the color and in the acidity, and by an increase in the pH. The inverted series G presents an exception to this rule in that these elements are almost completely precipitated in the lowest, acidic A_2 layer where the loss on ignition is increased, where the color remains unchanged and where the pH is low. Here, at least, the sesquioxides move to a large extent independent of the humus acidoids. The sesquioxides are evidently here precipitated (isoelectrically) by a combination with the strong acidoids in the A_2 layer. There is in this layer no basoids strong enough to combine with the humus acidoids which are, therefore, eluviated. Note that in system G 2, where the conditions are the reverse, the humus acidoids are precipitated (color = 0) while considerable aluminum is solvated.

From the results of the experiment we may conclude that aluminum and iron are cationically solvated by combining with acids with which they form dissociated compounds and that this solvation is in the order

$$\text{Fe (ous)} > \text{Al} > \text{Fe (ic)}$$

and that their single ions or cationic complexes are precipitated either by the interaction with acidoids or by encountering a higher pH.

Eluviation and illuviation. If we subtract the quantities of aluminum and iron removed from each layer from the quantities which entered the layer and plot the differences (+ and —) as in fig. 50 we get a good picture of the eluviated (lost) and illuviated (gained) amounts of the elements.

We shall ignore the minor deviations such as the secondary maxima. These might be real or they might be due to many causes of errors such as irregular percolation etc. It must be remembered that we have assumed that what happened in the layer whose sol-

vate we analysed also happened in the corresponding layer in the following lysimeters. A second maximum (observed in some instances in the case of aluminum) is, however, theoretically possible when, for example, aluminum is precipitated in one layer due to a high acidoid content (= low I. E. P.) and solvated in the next layer due to a high basoid content (= high I. E. P.) provided the pH in the latter case remains low enough.

It is interesting to note how a thick layer of humus causes the eluviation to penetrate into the B_1 material (fig. 50 A) and how the N. 0.01 $CaCl_2$ solution has the same effect to an even more

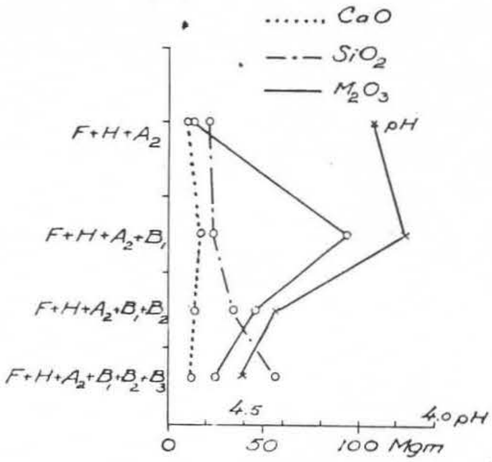

Fig. 52. The composition of the solvates from the mixed series (table 24 c).

exaggerated extent (fig. 50 D). In the latter case the bulk of the illuviation is pushed deep into the third B_3 layer.

With a moderate to thin humus layer the eluviation confines itself to the naturally eluviated material, the A_2 layer and the illuviation begins in B_1 (fig. 50 B and C). The use of a N. 0.001 $CaCl_2$ solution instead of water again causes a deeper penetration of the forces of eluviation (fig. 50 E_I and F).

Köhler (1941) puts the average Cl content of rain water, in the vicinity of the ocean, at about N. 0.0001. This is ten times lower than our lowest concentration of salt but then nature has more time at her disposal than we had in our experiment. Atmospheric (cyclic) electrolytes undoubtedly play a dominant role in soil formation.

According to Aaltonen (1939) the podzol B-horizon grows from the bottom upwards. He found, in other words, the maximum illuviation at a greater depth in young than in old profiles. Matt-

SON and LÖNNEMARK (1939) accounted for this on the basis of the theory of isoelectric weathering. Our series E_{II} might be looked upon as an infant podzol profile. It consisted originally exclusively of unpodzolized B_3 material. Now at the end of the experiment we might distinguish between an A_1, an A_2, and a B horizon, the latter with a maximum in the lowest layer exactly as postulated by AALTONEN (cf. fig. 51).

The explanation is that the unpodzolized layers were poor in acidoids and rich in basoids. The cationic sol complex had, therefore, a high I. E. P. and could wander deep down before it encountered a pH high enough to be precipitated.

Now it might be asked: why did not as much or more aluminum and iron solvate in the uppermost B_3 layer as in the second 150 gram layer since the former was in immediate contact with the humus layer? Our explanation is that humus acidoids got into the upper B_3 layer (note that the color changed from yellow to colorless) and stabilized the basoids through the formation of non-dissociating compounds thus lowering the I. E. P. of the gel complex. This is, in our opinion, the chemistry of the process which leads to the formation of the A_1-horizon in the podzol profile. The A_1-horizon is, for this reason, in general richer in sesquioxides than the A_2-horizon. This does not mean that the sesquioxides cannot be eluviated in the presence of much humus acidoids for even in the humus layer itself they can be solvated anionically in combination with the acidoids at high pH and by complete hydrolysis as free ions at low pH.

The eluviation and illuviation in the G series is also shown in fig. 51. This series resembles the E_{II} series in so far that the upper mineral layer also consists of the unpodzolized, basic B_3 material. The fact that the eluviation is here greatest in the upper mineral layer might be ascribed to the thick humus layer. We might here have the beginning of a humus podzol, that is, a profile in which the humus acidoids in the eluviated horizon dominate to such an extent that we get a black »Bleicherde». An interesting phenomenon in this series is the strong illuviation of the sesquioxides in the bottom A_2 layer. This might be looked upon as a regeneration of the brown earth material of the nature described by TAMM (1930). The acidoids in A_2 apparently precipitate the sesquioxides isoelectrically despite the low pH.

The H series cannot be presented graphically by the scheme employed in fig. 50 and 51 since each system represents a new mixture of all the components. Fig. 52 shows instead the composition of the solvates with respect to Si, Al+Fe, Ca and pH. The most notable is here the outstanding maxima in sesquioxides and calcium after the admixture of B_1, which also yields the lowest pH, and the marked increase in silica after the admixture of B_2 and

B_3. After the addition of B_3 the silica greatly exceeds the sesquioxides. The series changes from an intensive cationic eluviation (system $F+H+A_2+B_1$) to a dominantly anionic eluviation (system $F+H+A_2+B_1+B_2+B_3$). That is, the mineral soil complex becomes poorer in sesquioxides and richer in silica in the first case (*podzol type of weathering*) and becomes richer in sesquioxides and poorer in silica in the second case (*brown earth type of weathering*).

Applications to practice.

If we consider the different systems in series II to represent progressive depths of cultivation of a virgin podzol we can draw some interesting conclusions. If the sod which is turned over includes only the A_2 and the upper, acidic part of the B-horizon we must anticipate, at least a temporary, intensified podzolization with the resulting loss of bases including the sesquioxides. Due to the great mobilization of nutrients we might anticipate a few good crops but the depletion will be rapid and the soil will soon become poorer than it once was. If, on the other hand, we turn over the soil materials down to a considerable depth of the B-horizon then the acidoids of the upper horizons will be »neutralized» by the basoids of the lower horizons and the strong bases, such as calcium, will be more available for the suppression of the actual acidity. The whole soil will thus be stabilized and assume a character akin to the brown earth. We can not thus repair the losses of the past such as those of the various cations, it is true, but we shall incorporate a number of nutrient elements in a more available condition. Among these phosphoric acid will probably be one of the most important. Firmly fixed by the sesquioxides in the B-horizon as it is, it will now become available through a displacement by the soil acidoids of humus and silica. Because of the mutual »neutralization» of the acidoids and basoids the soil will require less time (cf. MATTSON and GUSTAFSSON 1935).

The good effect of »double digging» and of deep plowing has long been recognized. The excellent results obtained by Dr. K. A. HASSELBALCH, who plowed up sandy podzols to a depth of 60 cm in the western part of Denmark, might here be mentioned. The good effect of deep cultivation (in well drained soils) is probably much greater in highly differentiated soils having a steep acidoid-basoid gradient such as the podzols than in the less differentiated soils such as the tshernozems.

The increased fertility of a »rested» soil is undoubtedly in part due to the establishment of new gradients such as the acidoid-basoid and the oxidation-reduction gradients which, when again disturbed give rise to renewed chemical and biological activities.

The pedosphere is like a living body. Its anatomical parts are represented by the great soil groups, its morphology by the profile characteristics, its histology by the texture and textural aggregates, its protoplasm by its colloidal complex and its physiology by the soil solution. The constitution of the pedosphere is adapted to the natural environment, the adjustment tending to be such that the prevailing forces of nature produce the least possible change in the soil.

This the largest of all organized bodies on the earth »lives» in a symbiotic relationship with all living things and by a continuous readjustment keeps the organic cycle going. Man is the only parasite of the soil for he continuously keeps bruising its tissue. But the tissue of the soil possesses, like all other tissues, the ability of healing. The plowing of the soil amounts to an injury of the soil tissue and a cultivated soil is a soil which continuously undergoes the process of healing.

When a soil is tilled there is a mingling of materials which possess different chemical affinities, new interfacial potentials are established, the activity is increased, some substances are solvated and carried away, others are brought in and precipitated and the whole process is directed toward a reestablishment of the more stable adjustment as dictated by the environmental conditions. The activity released during this process of healing is to a large measure responsible for the fertility of the soil which, augmented by the application of fertilizers may be perpetuated.

The processes taking place in the cultivated soil belong to the realm of agro-pedology, a discipline which, as JOFFE says, is still waiting for its master architect. We believe that a comparative study of the interactions of soil materials in the undisturbed (as far as this is possible) and in the mixed condition would serve to throw much light on agro-pedological processes.

Summary.

The solvation and precipitation in podzolic materials have been studied in laboratory lysimeters by placing samples from the various soil horizons in layers in large filter tubes and leaching with water and with dilute salt solutions. In one series the samples were mixed as when the soil is cultivated.

In the layered series there was an eluviation of dark colored organic matter and of sesquioxides from the acidic upper layers and an illuviation in the lower B-horizon layers which are rich in basoids and have a higher isoelectric point. The most basic layer from the B_3 horizon adsorbed the solvates most efficiently.

In the mixed series there was a great solvation in the mixtures

from the upper soil horizons but when the lower B horizon materials were included the systems showed a much greater stability.

The theory of isoelectric weathering has been applied to account for the phenomena and the practical applications have been discussed.

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